

ORIGINAL MINERALOGY OF TRILOBITE EXOSKELETONS

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ABSTRACT. The mineralized exoskeletons of well-preserved trilobites are now composed of low-magnesian calcite. However, as this is the only form of calcium carbonate to survive in Lower Palaeozoic rocks, such a mineralogy may be a function of diagenetic processes rather than reflecting primary cuticle composition. Ferroan calcite replacement has previously been used to infer an original high-magnesian calcite mineralogy for trilobite exoskeletons. By contrast, petrographic data involving over seventy trilobite species, ranging in age from Cambrian to Devonian, together with carbon and oxygen stable isotope analyses of specimens from the Much Wenlock Limestone Formation, England (Wenlock), are here used to infer that trilobites constructed low-magnesian calcite exoskeletons. Petrographically, the trilobite cuticles share the same preservational characteristics as low-magnesian calcite organisms such as articulate brachiopods. They also have very similar isotopic signatures to those of brachiopods, yet differ from crinoids which secreted high-magnesian calcite ossicles and now commonly contain microdolomite inclusions and secondary voids. Together, these separate lines of evidence strongly suggest that trilobite exoskeletons originally had a low-magnesian calcite mineralogy.

MOST trilobites had heavily mineralized exoskeletons, a characteristic shared by some other marine arthropods such as decapod crustaceans, cirripedes, and ostracodes. Three trilobite species with entirely organic cuticles have been described (Whittington 1977, 1985; Dzik and Lenzion 1988), but this paper is concerned only with those trilobites that had mineralized exoskeletons. In such trilobites the dorsal exoskeleton and hypostome were predominantly composed of calcium carbonate with a small proportion of organic matter. If the exoskeleton is decalcified in EDTA, the remains of the organic framework become apparent as a delicate brown residue of unknown composition still retaining the general structure of the cuticle (Dalingwater 1973; Teigler and Towe 1975; Miller 1976; Dalingwater and Miller 1977). The ultrastructure of the exoskeleton comprises an outer prismatic layer with a much thicker principal layer below (text-fig. 1*d*). Several types of cuticular microstructure may also occur, including laminations, tubercles, and canals (Dalingwater 1973; Miller 1976; Størmer 1980; Mutvei 1981). Despite increasing understanding of the structure of the exoskeleton, its original mineralogy has not previously been determined.

Marine invertebrates construct their exoskeletons from a variety of forms of calcium carbonate. Scleractinian corals use aragonite (A), echinoderms have high-magnesian calcite (HMC) hard parts ($> 5\%$ MgCO_3), and articulate brachiopods construct low-magnesian calcite (LMC) valves ($< 5\%$ MgCO_3); sometimes combinations of these may be used, as in certain molluscs (Milliman 1974; Wolf *et al.* 1976; Morrison and Brand 1987). Among modern arthropods, decapod crustaceans utilize HMC and small amounts of calcium phosphate, whereas most ostracodes use LMC, and cirripedes form their lateral plates from LMC with some species having A basal plates (Richards 1951; Milliman 1974; Morrison and Brand 1987).

When trilobite exoskeletons are well preserved and still exhibit primary microstructures, examination of stained thin-sections and X-ray diffraction show they are composed of calcite (Dalingwater 1973; Teigler and Towe 1975). Analyses by microprobe (Teigler and Towe 1975; Miller and Clarkson 1980) indicate an LMC mineralogy.

Isolated reports of phosphate within trilobite cuticle (Dalingwater 1973; Teigler and Towe 1975) probably represent secondary deposits. An LMC mineralogy is to be expected for Palaeozoic fossils, for although the primary composition of extant organisms or well-preserved Tertiary fossils can be determined directly, the older the fossil the more likely is its composition to have been

altered by diagenetic processes. The original composition of Lower Palaeozoic fossils may be inferred by comparisons with living taxa of the same class, from petrographic evidence (Lohmann and Meyers 1977; Richter and Füchtbauer 1978), and from stable isotope data. These principles are used for trilobites, which have no close modern relatives and, in the following sections, data are presented which indicate an original LMC mineralogy.

MATERIAL AND METHODS

As part of a wider study on trilobite cuticles, examples of over seventy species of trilobite, ranging in age from Cambrian to Devonian, were embedded in Araldite (epoxy resin) and made into uncovered thin-sections. They were then examined by cathodoluminescence, using a Technosyn cold cathode luminoscope, model 8200 Mk11, at a gun current of 15–18 kV and 400–600 mA. The thin-sections were later stained (Dickson 1966) and protected by coverslips before examination in transmitted light.

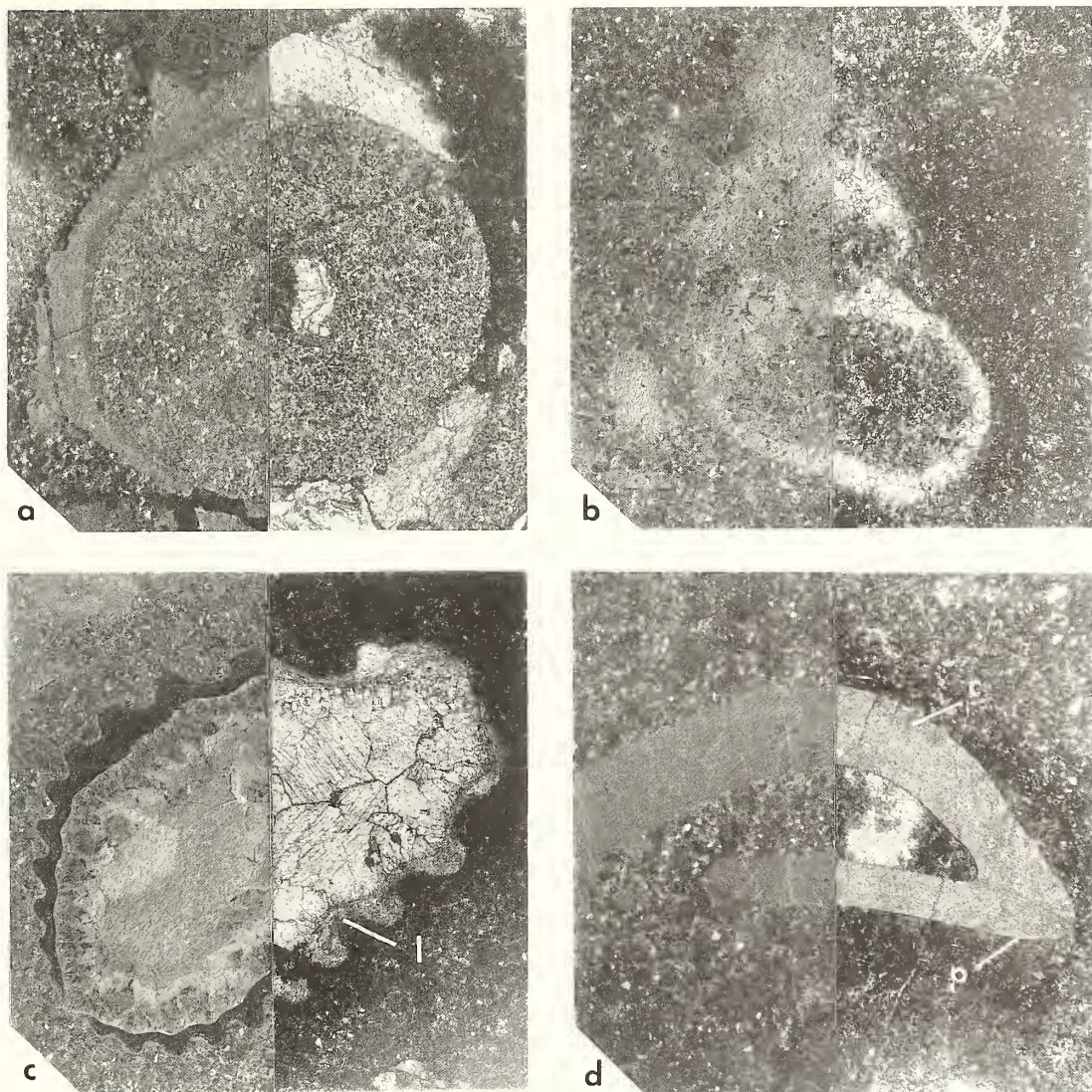
Ten samples of five trilobite species from the Much Wenlock Limestone Formation, England (Wenlock) were prepared for atomic absorption analyses. Unweathered specimens were scraped with a scalpel to obtain approximately 50 mg of exoskeleton in powder form. Each sample was then dissolved in 10 ml of concentrated HCl diluted by 50%, and boiled on a hot plate for 2 min until the solution became clear, adding more distilled water as necessary. The solutions were allowed to cool and made up to 100 ml volume with distilled water, before running on a Perkin-Elmer atomic absorption spectrophotometer, model 460.

Pieces of trilobite cuticle, brachiopod valves, and individual crinoid ossicles from the Much Wenlock Limestone Formation were prepared for carbon and oxygen stable isotope analyses. Unweathered specimens were scraped with a scalpel to obtain 5 mg of powder, great care being taken to avoid contamination from the surrounding matrix. Isotopic ratios were then obtained following established methods (McCrea 1950). All isotopic values are in parts per million with respect to PDB (Pee Dee Belemnite). Precision is around 0.1% (1 σ) or better for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

PETROGRAPHY

Trilobite exoskeletons are best preserved in dark, fine-grained limestones and calcareous mudstones. Fine primary microstructures, such as canals and laminations, are often retained in such cases and eye lenses may remain capable of focussing sharp images (Towe 1973). Loss of most primary structure is inevitable during the inversion of aragonite to calcite. Occasionally, traces of organic inclusions outline former structures and produce pseudopleochroic calcite in neomorphically altered aragonite (Hudson 1962). As the preservation of trilobite exoskeletons is generally much better than this, a primary A mineralogy can be discounted.

Richter and Füchtbauer (1978) suggested that replacement by ferroan calcite is indicative of a former HMC composition, as LMC is more stable and therefore not replaced. Trilobite cuticles are very occasionally preserved in this way. The former existence of HMC can also be indicated by the presence of microdolomites that formed in a closed system during the conversion to LMC (Lohmann and Meyers 1977). During this process the excess magnesium ions which are not incorporated into the LMC lattice form microdolomite inclusions 1–10 μm in diameter, which are readily identified with cathodoluminescence. Microdolomites have never been found within trilobite exoskeletons, despite the latter commonly occurring in close association with inclusion-rich components, suggesting that they may have had an original LMC mineralogy. These differences are well illustrated by petrological examination of fossils from the Much Wenlock Limestone Formation, which show clear preservational variations between taxa (text-fig. 1). Gastropods which had an original A exoskeleton have been replaced by a void-filling cement (Bathurst 1975) with total loss of primary microstructure. Crinoid ossicles, originally HMC, have abundant microdolomite inclusions and often contain secondary voids. Both brachiopods (primary LMC) and trilobites show good preservation, with laminae and canals still visible. Neither taxon ever has any microdolomite inclusions or shows evidence of secondary dissolution—suggesting that they were both composed of LMC.



TEXT-FIG. 1. Composite photomicrographs of fossils from the Much Wenlock Limestone Formation. In each case, the left-hand side is taken under cathodoluminescence (CL) and the right-hand side under plane polarized light (PPL). *a*, crinoid ossicle, NMW 88.22G.1, originally HMC, now with syntaxial overgrowth. Internally the ossicle has become coarsely crystalline, and under CL, small bright points mark the positions of microdolomites which formed during the conversion to LMC. $\times 25$. *b*, gastropod, NMW 88.22G.2, originally A which has now been totally replaced by a coarse, clear, void-filling cement. $\times 30$. *c*, strongly ribbed brachiopod, NMW 88.22G.2, primary LMC retaining its original structure of fine laminations (l). Under CL the brachiopod is non-luminescent and contains no microdolomite inclusions unlike the surrounding matrix. $\times 30$. *d*, trilobite cuticle, NMW 88.22G.2, with thin, outer prismatic layer (p), and fine canals (c) within small tubercles, still visible under PPL. Under CL the exoskeleton is weakly luminescent, a function of its trace element content, but no microdolomites are present. $\times 40$.

ATOMIC ABSORPTION ANALYSES

Average composition of ten trilobite specimens from the Much Wenlock Limestone Formation, England—localities 43 and 64 of Thomas (1978)—were as follows:

%Ca ²⁺	%CaCO ₃	%Mg ²⁺	%MgCO ₃	Total CaMgCO ₃	%Fe ²⁺
35.18	87.94	0.81	2.82	89.89	0.50
±2.73	±6.81	±0.57	±1.98	±6.83	±0.19

(Impurities such as organic matrix, ferroan calcite, pyrite, and water account for incomplete percentage totals.)

These data indicate an LMC mineralogy.

CARBON AND OXYGEN STABLE ISOTOPE ANALYSES

The principles involved in carbon and oxygen isotope analyses are outlined below; for a more detailed introduction to stable isotopes and their geological uses, see Hoefs (1980) and Arthur *et al.* (1983). The isotopic fractionation of oxygen between calcium carbonate and water is temperature-dependent (McCrea 1950). Although the isotopic composition of meteoric waters (as measured from atmospheric precipitation) varies considerably with temperature, altitude, and latitude, the isotopic composition of sea-water remains relatively constant at a given temperature because of its much larger mass. It would be expected that marine invertebrates secreting a calcium carbonate exoskeleton would do so in isotopic equilibrium with the surrounding sea-water. This is the case in certain organisms, such as articulate brachiopods and Recent cirripedes, though other groups such as echinoderms exhibit a 'vital effect' and secrete exoskeletons that are not in isotopic equilibrium. This non-equilibrium is thought to result from variations in their physiological processes, such as use of metabolic carbon dioxide (Milliman 1974; Morrison and Brand 1987). Hence different marine invertebrate groups possess distinctive 'isotopic signatures', related both to the temperature of the sea-water they inhabit and to their physiology. In general, forms with LMC exoskeletons tend to be in isotopic equilibrium, whereas those secreting A or HMC hard parts show a vital effect.

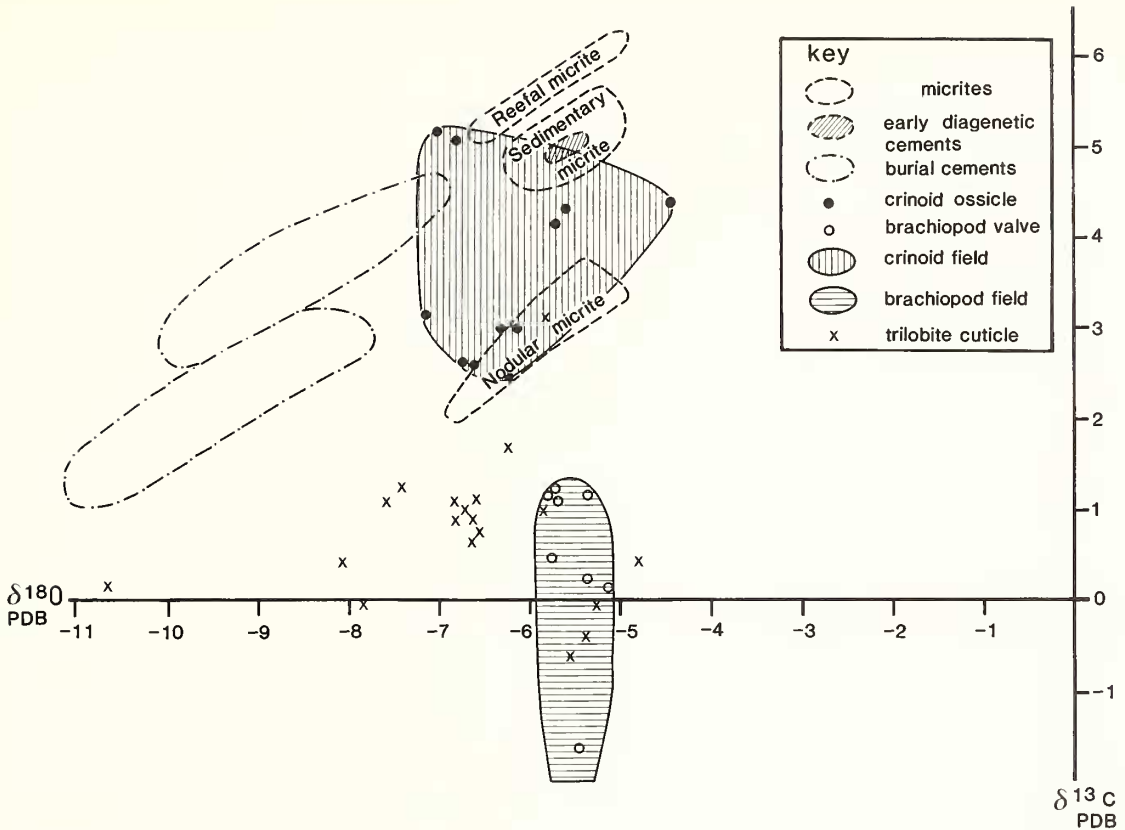
Isotopic signatures can be determined for fossils and coexisting inorganically precipitated carbonate, including cements. For any locality the relative differences in carbon and oxygen isotopic values between organisms and the sea-water at the time of their formation should still be apparent, even with diagenetic effects superimposed, provided the components did not reach isotopic equilibrium with pore fluids.

On this basis the composition of trilobite exoskeletons was determined using specimens from the Much Wenlock Limestone Formation, which contains some of the best-preserved trilobites in Britain. Conodont elements from this formation have suffered very minor thermal maturation, 50–90 °C (Aldridge 1986), suggesting burial to only 1–1.5 km. Previous carbon and oxygen isotope studies from this formation (Ratcliffe 1987) revealed a clear distinction between the isotopic values of brachiopods and crinoid ossicles. These data from primary and secondary LMC are then used here for comparison with the isotopic signature obtained from trilobite cuticles.

Discussion

The isotope data (text-fig. 2) show no relationship between the trilobite species used, or the locality from which they came. The trilobite data plot much more closely to the brachiopod values than to the other limestone components, and the spread of points can be explained when viewed in relation with the diagenetic history of the formation (Ratcliffe 1987).

All originally unstable components now have elevated $\delta^{13}\text{C}$ signatures relative to Silurian marine carbonates. Similarly, early diagenetic primary LMC cements have relatively high $\delta^{13}\text{C}$



TEXT-FIG. 2. Carbon and oxygen stable isotope compositions for allochems and cements from the Much Wenlock Limestone Formation. Based partly on unpublished data from K. T. Ratcliffe.

values. These elevated values reflect the development of early diagenetic pore fluids, so the more porous the constituent analysed, the more cement it will have incorporated, influencing the net isotopic value obtained. The micrites all have relatively high $\delta^{13}\text{C}$ values compared with the brachiopods, which were in isotopic equilibrium with the sea-water (Lowenstam 1961; Popp *et al.* 1986). This is probably because they include small amounts of early diagenetic cements with a high $\delta^{13}\text{C}$ value. They also show a north-east/south-west trend similar to that of the burial cements, again indicating incorporation of burial cement in the micrite micro-pores. Crinoid ossicles also have high $\delta^{13}\text{C}$ values, but with a relatively wide distribution. The composition of these originally HMC skeletal parts is a reflection of their original isotopic signature, and partial equilibration with the pore fluids that generated the early diagenetic primary LMC cements.

The brachiopods, being primary LMC and hence very stable, have low $\delta^{13}\text{C}$ values. They also show very little spread in data due to their low porosity. These factors give brachiopods great stability, making them suitable for palaeotemperature determinations. The trilobite cuticles also have low $\delta^{13}\text{C}$ values and are distinct from both the micritic and cement phases, suggesting that they, like the brachiopods, were constructed from LMC. Trilobite exoskeletons contain numerous canals which were liable to being infilled by either early cements or burial cement, the degree to which this happened being reflected in the variation of their isotopic values. When these effects are taken into account, it can be seen that the isotopic signature of trilobites was originally very similar to that of the brachiopods: close to isotopic equilibrium with sea-water.

The degree of porosity within trilobite exoskeletons makes them unsuitable for palaeotemperature determinations despite their primary LMC mineralogy; eye lenses are a possible exception. Similar problems arise in using belemnite rostra for this purpose (Veizer 1974). It is notable that the isotopic composition of Silurian sea-water obtained from these data is lower in $\delta^{13}\text{C}$ than previously published results from the Silurian of Gotland (Frykman 1986). However, as the $\delta^{18}\text{O}$ values are in the same range, implying the same temperatures, this is probably due to differing productivity levels between England and Gotland.

The present study emphasizes that fossils should not be studied in isolation, since the isotopic values of the trilobite specimens can only be interpreted when viewed in conjunction with data from other limestone allochems and cements. Only in this way can diagenetic effects be identified and their influences evaluated.

CONCLUDING REMARKS

Comparison of the petrographic and chemical characteristics of taxa of known mineralogy with those of trilobites occurring in the same samples strongly suggests that mineralized trilobite exoskeletons were constructed from LMC. This contrasts with Richter and Füchtbauer's (1978) inferred HMC composition based on replacement by ferroan calcite. However, this type of replacement in trilobites is very rare and probably results merely from local diagenetic conditions. Where ferroan calcite trilobites have been found in the Much Wenlock Limestone Formation, they occur in a ferruginous crinoidal grainstone lithofacies which had major diagenetic interaction with nearby iron-rich mudstones (Ratcliffe 1987), so that the vast majority of the other limestone components have been affected. Trilobite cuticles were basically stable, being composed of LMC, but nevertheless subject to alteration by highly reactive pore fluids. Microstructure (Walter 1985) and the amount and composition of the organic matter within the exoskeleton all influence the rate of ionic exchange. Even brachiopods, which are recognized as having had a LMC composition, may occasionally be replaced by ferroan calcite (A. M. Searl, pers. comm.). The total absence of microdolomites from trilobite cuticles, the absence of secondary voids, and the similarity in type of preservation and isotopic composition between trilobites and brachiopods, indicate that trilobites have a primary LMC mineralogy. Given the early appearance of trilobites in the Phanerozoic record, this is compatible with the general evolutionary trend of biomineralization. This began with a brief use of calcium phosphate in the Tommotian followed by a change to carbonate—first LMC, then HMC—until today the majority of marine organisms use A (Wilkinson 1979; Lowenstam 1981; Lowenstam and Weiner 1983).

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